



Prediction of Volatile Losses from Contaminated Exposed Sediments

by C. Price, J. Brannon, S. Yost, R. Ravikrishna, K. T. Valsaraj

PURPOSE: This technical note describes laboratory and field investigations conducted to obtain flux data from contaminated dredged materials for the emission of volatile organic chemicals (VOCs) from sediment exposed to the atmosphere. These data have been used to develop and validate predictive volatile emissions models. Laboratory and field results and predictive equations are presented.

BACKGROUND: One potential pathway of contaminant migration from a confined disposal facility (CDF) is volatilization of volatile and semi-volatile compounds. Disposal and storage operations associated with placement of dredged material in CDFs can increase the opportunity for volatile emissions.

Previous laboratory investigations conducted at the Engineer Research and Development Center, Waterways Experiment Station (WES) with New Bedford Harbor, Massachusetts, sediment showed large amounts of VOCs emitted when the material was disturbed and underlying sediment layers exposed to air (Thibodeaux 1989). More recent investigations with sediments from Indiana Harbor Canal (IHC) and Grand Calumet River, Illinois, also revealed similar behavior with increased emissions of polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) after the sediments were reworked and fresh sediment was exposed to the atmosphere (Price et al. 1998, 1999; Valsaraj et al. 1999). Methods for predicting volatile losses from sediment during the different aspects of dredging, disposal, and site management are needed to develop guidelines for controlling possible volatile emissions from contaminated dredged materials.

INTRODUCTION: Dredging, disposal, and site management operations at CDFs can increase the potential for volatile emissions from contaminated sediments. Valsaraj, Thibodeaux, and Reible (1995) surveyed the potential sediment-to-air mass transfer pathways for volatile compounds and found the primary locale for emissions to be from exposed sediment. Sediment physical characteristics, such as moisture content, porosity, aging, and percent oil and grease can play a significant role in controlling volatile contaminant losses. Environmental factors such as relative air humidity and temperature can also affect emissions. Compound chemical characteristics such as Henry's Law Constant and vapor pressure also play important roles in determining volatility from a sediment.

Initial research efforts focused on generating laboratory data from laboratory-spiked and field sediments to validate proposed mathematical models for estimating volatile emissions from contaminated sediments (Thibodeaux 1989). These results are presented in several technical notes and journal articles (Price et al. 1997, 1998, 1999; Valsaraj et al. 1997, 1999; Ravikrishna et al. 1998). To verify laboratory results and predictive equations, a controlled field simulation experiment was conducted with a contaminated sediment that was used in a previous laboratory investigation.

MATERIALS AND METHODS:

z **Sediment.** Sediment from IHC was used in the controlled field verification experiment. This sediment was used because of existing laboratory data on volatile emissions (Valsaraj et al. 1999; Price et al. 1999). The properties of this sediment are presented in Table 1, and sediment analytical results for 17 PAH compounds are listed in Figure 1. For model validation and experimental purposes, three compounds were chosen as representative VOCs due to their prevalence in contaminated sediments; phenanthrene, pyrene, and dibenzofuran.

Table 1 Physical and Chemical Properties of Indiana Harbor Canal Sediment	
Property	Value
Moisture content	49
Percent sand	45
Percent silt	46
Percent clay	8
Percent total organic carbon	6.9
Percent oil and grease	0.94
Porosity, cm ³ /cm ³	0.78
Bulk density, g/cm ³	0.6

z **Flux chambers.** All volatile emission measurements in the field were conducted with a modified VOC flux chamber used in laboratory experiments (Price et al. 1998) (Figure 2). The two-piece aluminum anodized chamber was designed by Louisiana State University (LSU), Chemical Engineering Department and constructed at WES and LSU. The chamber was designed to sample a 375-cm² area of sediment. The bottom of the chamber was open and fitted with knife-blade-edged panels that could be pushed into the sediment to form a seal over the sediment surface. The bottom and top of the chamber were sealed with an O-ring and threaded fasteners for an airtight fit. The space between the sediment and the surface of the flux chamber was 1 cm.

Contaminant-specific adsorbent-filled air sampling tubes (Orbo 44, Supelco Inc., PA) were attached to the chamber exit port. Traps were removed from the exit line at the end of each sampling interval, and solvent was extracted and analyzed according to U.S. Environmental Protection Agency (EPA) method 8270 (USEPA 1982). The laboratory procedures used and applied in the field experiments are described in Price et al. (1997). Methodology was identical to that in the laboratory, except that air was applied over the sediment surface. The carrier air in the field experiments was pulled with a vacuum instead of having compressed air pushed over the sediment surface.

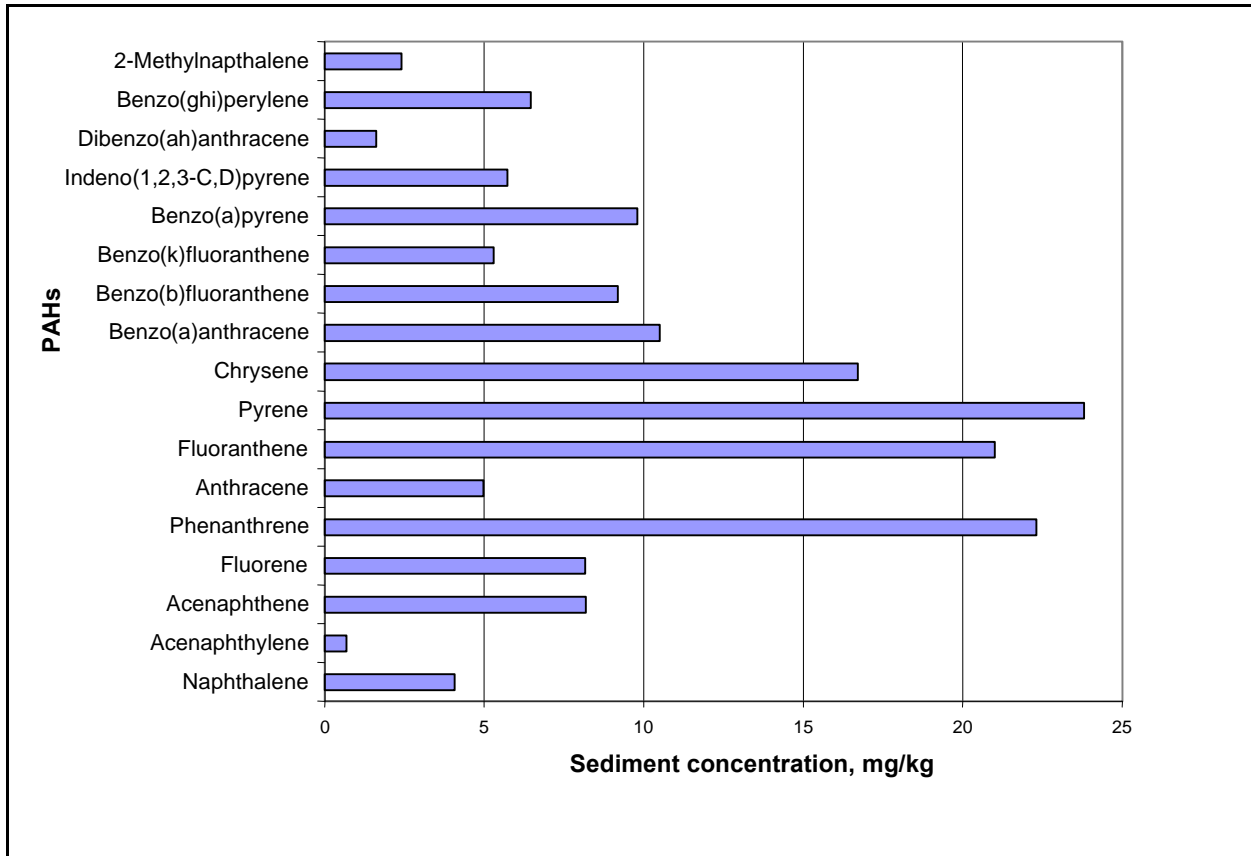


Figure 1. Initial concentration of PAHs in IHC sediment

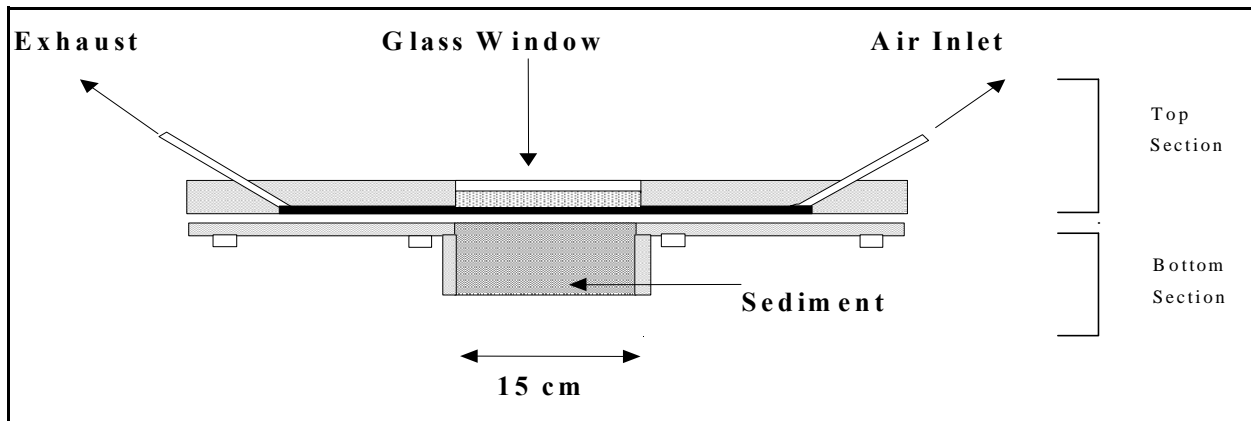


Figure 2. Schematic of flux chamber for measuring volatile emissions in the field

Contaminant flux [$N_A(t)$] through the chamber was calculated by determining the total mass of material captured in a given time interval using the equation

$$N_A(t) = \frac{\Delta m}{\Delta t A_c}$$

where

m = mass (ng) of compound collected on the trap in time t (hr)

A_c = area of the sediment-air interface, cm^2

$N_A(t)$ is expressed in $\text{ng}/\text{cm}^2/\text{hr}$

Controlled Field Simulation Site. Figure 3 is a schematic of the outdoor facility used for flux measurements in the field. The sediment was contained in a 4-ft by 4-ft by 2-ft wooden chamber (lysimeter) that was buried in the ground to the top level of the chamber. An underdrain was constructed in the bottom of the chamber to remove any excess water and an overflow drain was also provided to remove any ponded water that may have collected after a rain event. Leachate and overflow water were collected onsite for proper disposal. A meteorological station that monitored sediment temperature, moisture, air temperature and relative humidity, wind speed and direction, and solar radiation was also available onsite. A 3-ft-high cover constructed of translucent fiberglass sheeting was placed over the lysimeter to prevent excess rainfall on the sediment, which would result in release of material from the chamber.

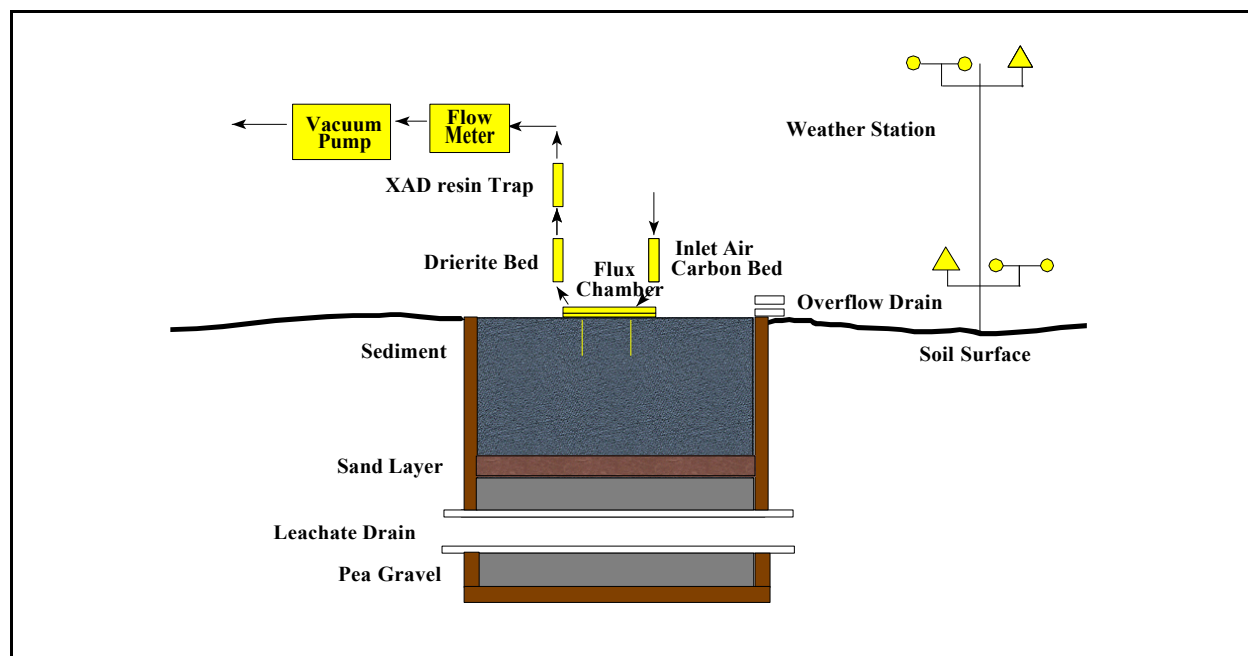


Figure 3. Pilot scale experimental schematic

Field Simulation Design. Eleven 20-gal containers of Indiana Harbor sediment were immediately consolidated upon arrival at WES. The sediment was loaded into the lysimeter the following day and immediately monitored for PAH emissions. Air was pulled through the adsorbent traps at 1.7 L/min with a vacuum pump. Figure 4 shows the flux chamber emplaced on the sediment 4 days after initial placement.

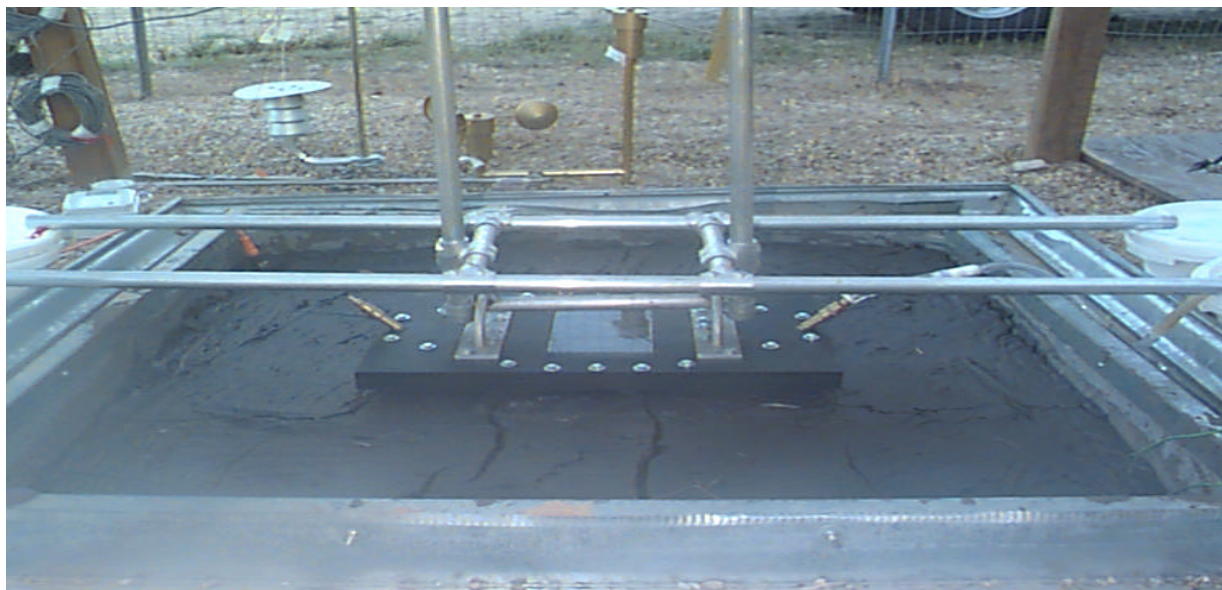


Figure 4. Flux chamber for sampling in the field

A single area on the sediment surface was sampled over a period of 78 hr in which five samples were taken at intervals of 6, 18, 42, 66, and 78 hr. After each sampling period, the trap was replaced with a new trap. After the 78-hr sample, the chamber was moved to a different section of the sediment surface and 24-hr samples were withdrawn over a 2-½-month period in order to randomly sample the overall 16-ft² sediment surface over time. The flux chamber was removed from the sediment when air samples were not being taken.

Two rainfall events were then applied to the overall sediment surface using a portable rainfall simulator (Price, Skogerboe, and Lee 1998). Reverse osmosis water (RO), collected from a system available at WES, was applied over the sediment at a rate of ½ in./hr for 30 min. Flux measurements were taken before and after this event. A second rainfall simulation was conducted in order to ensure that the sediment surface was completely saturated and another flux measurement was made. The sediment surface was later reworked to expose fresh material to the atmosphere and flux was measured before and after mixing.

A laboratory experiment was also conducted with the same sediment used in the field simulation to verify previous laboratory results. The laboratory flux chamber and experimental design are discussed in Price, Skogerboe, and Lee (1998).

RESULTS AND DISCUSSION:

z Flux Measurements: Initial fluxes of various PAHs are given in Table 2 and represent the first 3 days of sampling. Of the 17 compounds present in the sediment, 6 exhibited a measurable flux.

PAH fluxes from Indiana harbor sediment showed flux behavior similar to previous experiments conducted with sediment collected from the same harbor. Fluxes rapidly decreased to a low level within the first 3 days of sampling. This behavior has been noted in previous laboratory experiments

conducted with sediments from other sites as well (e.g., Indiana Harbor, Grand Calumet River, and New York Harbor) (Price, Skogerboe, and Lee 1998, 1999; Ravikrishna et al. 1998; Valsaraj et al. 1999).

Table 2 Initial PAH Fluxes (ng/cm²/hr) from the Pilot Scale Field Test			
Hydrocarbon	6-hr Sample	24-hr Sample	72-hr Sample
Naphthalene	7	6	1
Phenanthrene	12	4	<1
Fluoranthene	20	7	<1
Pyrene	7	2	<1
Benzo(b)fluoranthene	2	<1	<1
Benzo(a)anthracene	4	<1	<1

Phenanthrene was chosen as the tracer compound for discussion due to the fact that extensive data from earlier flux experiments are available for comparison. Phenanthrene emissions from Indiana Harbor Canal sediment in the field lysimeter and in laboratory flux chambers showed similar trends (Figure 5). In the field experiment, phenanthrene flux decreased from 4.0 to 0.17 ng/cm²/hr 68 hr after the sediment had been placed in the lysimeter. In the laboratory experiment, fluxes were similar (0.11 ng/cm²/hr) to those observed in the field experiment 72 hr after sediment was placed in the chamber.

Sediment rewetting did not increase emissions in either the field or laboratory. This is probably due to the fact that the sediment surface never became dry. Previous laboratory experiments with Indiana Harbor sediment showed that the sediment moisture did not significantly decrease over time and that the relative humidity in the exit air passed over the sediment surface did not decrease. This would account for the lack of an increase in flux rates after water was applied to the sediment surface. Typically, rewetting of a dry sediment decreases sediment sorptive capacity for volatile contaminants, resulting in an increase in flux, but this was not observed here.

Phenanthrene fluxes increased from 0.20 to 3.0 ng/cm²/hr following reworking of the sediment in the field experiment. Similar increases in PAH fluxes were observed following reworking in previous laboratory experiments conducted with both Indiana Harbor and Grand Calumet River sediments. Reworking exposes fresh material from the lower layers, increasing the surface vapor concentration of compounds, thus resulting in increased fluxes for a short period. After the first few hours of exposure, the surface of a sediment is quickly depleted of volatile compounds and contaminant transport becomes sediment-side-controlled since contaminants must diffuse from lower layers. These results indicate that field simulations and laboratory experiments showed similar trends in volatile emissions of PAHs following rewetting and reworking of the sediment.

z Model Description: Predictive equations have been developed to address volatile emissions from exposed sediments. Laboratory experimental data produced at WES and LSU were used to

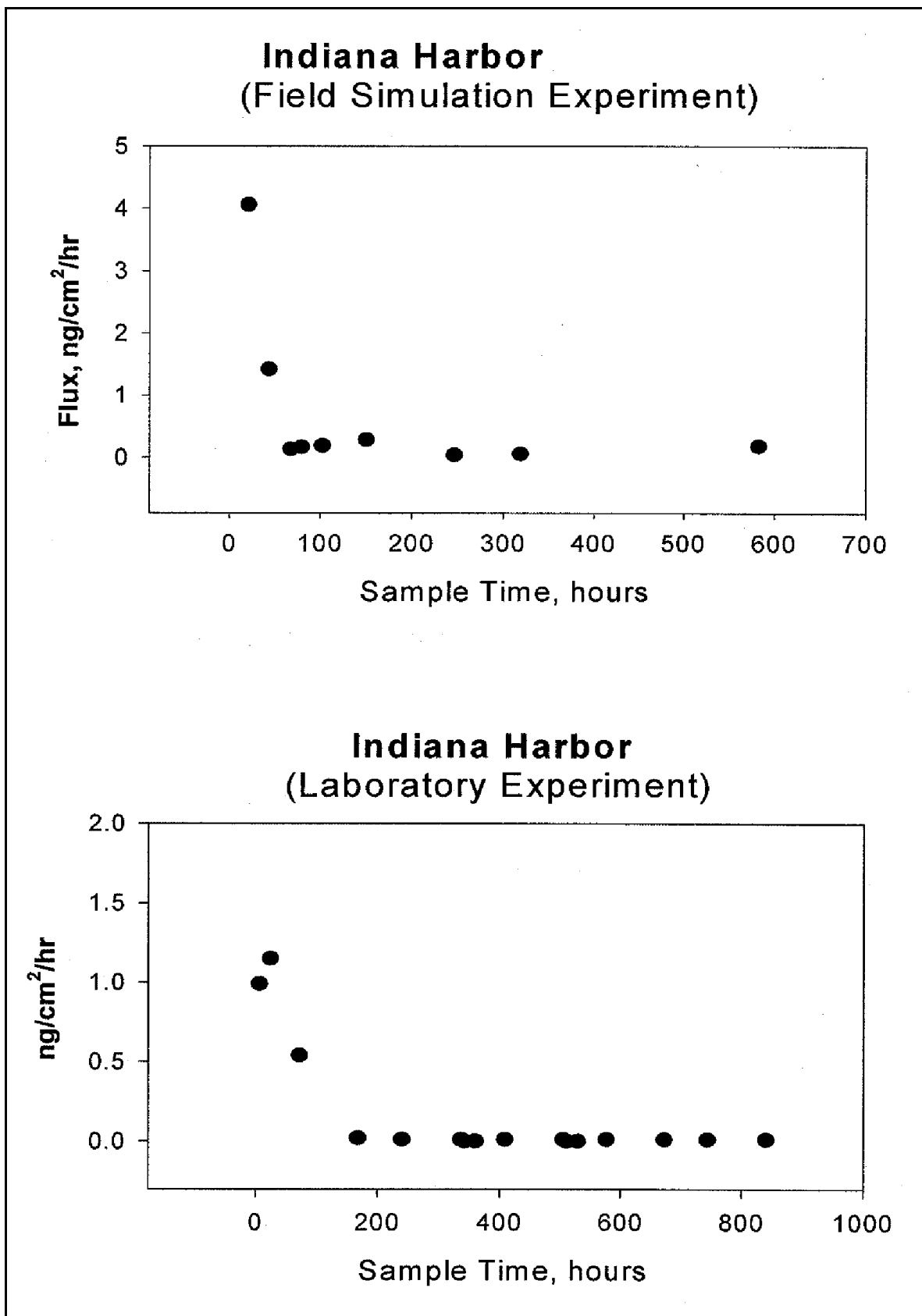


Figure 5. Phenanthrene fluxes from field and laboratory studies

develop and verify these equations. The chemodynamic model and analytical equations used in describing all laboratory and field volatile emission data are detailed in Valsaraj et al. (1999) and Choy and Reible (1999).

Contaminants are transported from sediment to air in a series of three steps (Valsaraj et al. 1999): (1) transport initiates with uniform loading of the contaminant onto the solids with the contaminant existing in equilibrium with the sediment pore air, (2) the contaminant diffuses through the air-filled pore spaces to the sediment-air interface, and (3) final convective transport occurs through the air-side boundary layer before the contaminant emerges into the bulk air. This describes a particle-to-air phase partitioning, which is then followed by two mass transport resistances before a contaminant enters the atmosphere; (1) initially compound resistance is completely on the air side, but with time, (2) the resistance becomes more sediment-side controlled as the contaminants diffuse up through the sediment from lower layers.

The model in Figure 6 considers a uniformly contaminated sediment that is freshly deposited in a CDF. Evaporation begins in the upper segments of the sediment and as volatile contaminants are depleted, the flux-to-air values decrease. This model is currently being modified at WES prior to incorporation into the Automated Dredging and Disposal Alternatives Modeling System (ADDAMS) suite of models currently available through the Waterways Experiment Station at: <http://www.wes.army.milel/elmodels/index.html#addams>.

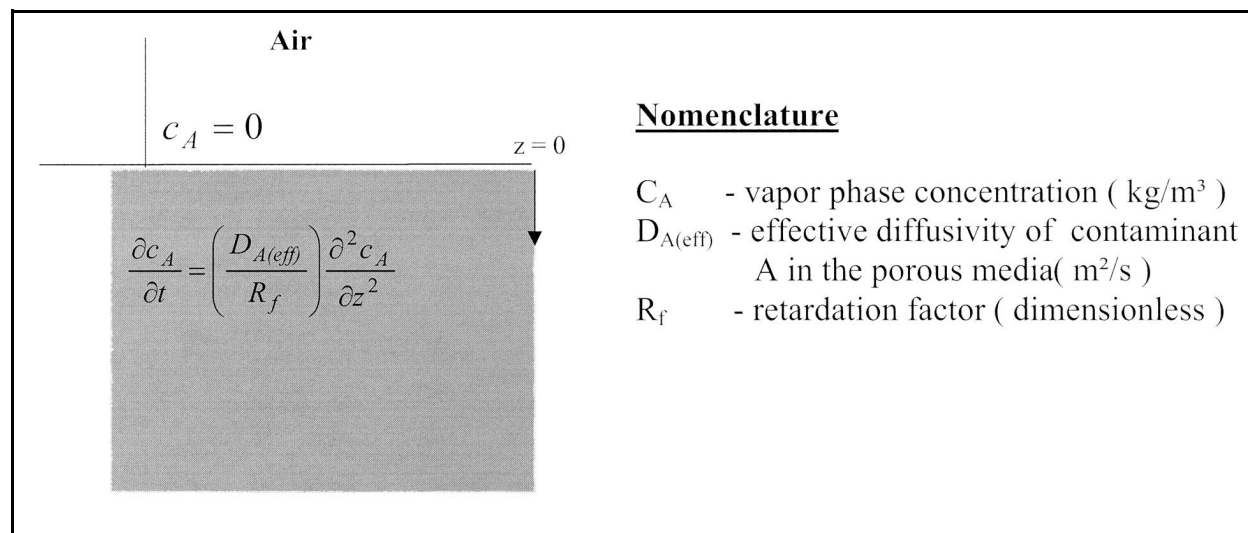


Figure 6. Schematic of the system for modeling

The model prediction for phenanthrene is compared to both the field simulation and laboratory experimental data in Figure 7. Under all three conditions, fluxes fell to below 1 ng/cm²/hr in the first few days after placement. It can be seen that the model predictive fluxes are in good agreement with the experimental data collected.

CONCLUSIONS: Results of these investigations revealed that the flux data obtained from the field simulation experiment exhibited trends similar to fluxes seen in the laboratory. The highest

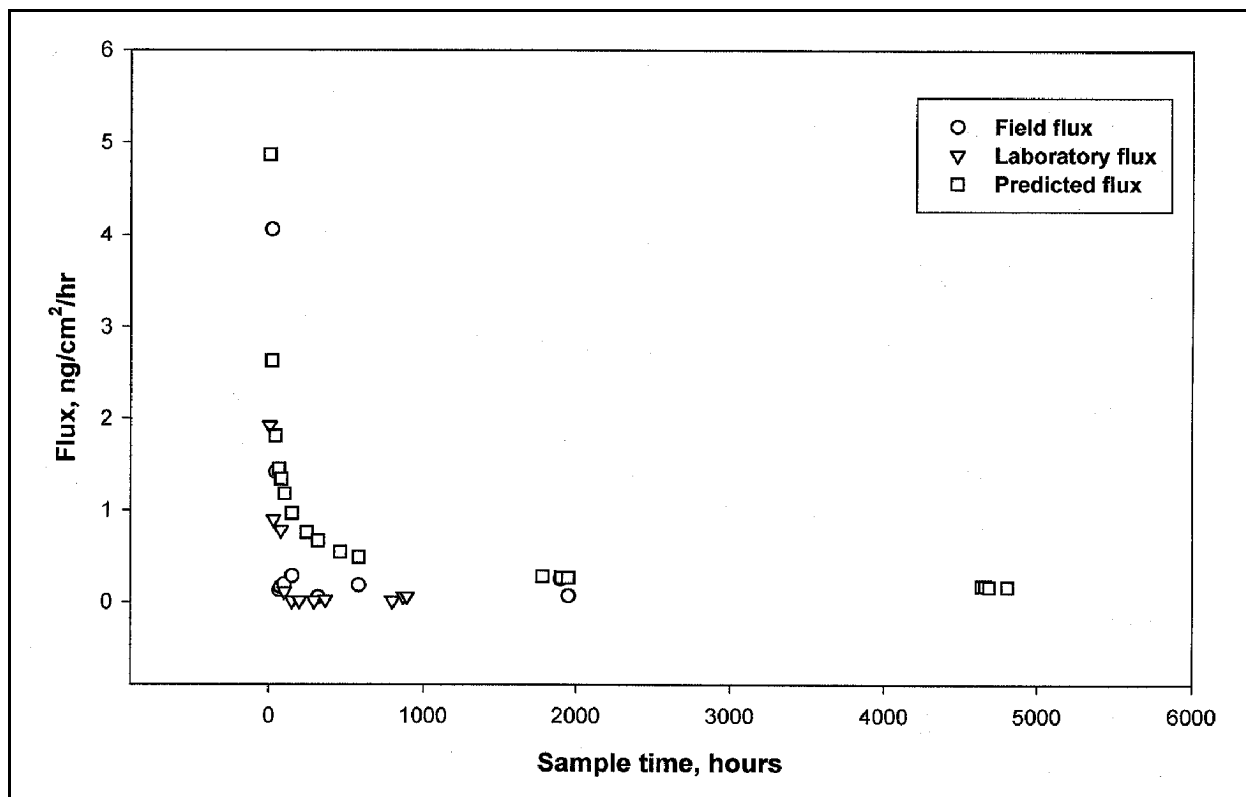


Figure 7. Experimental data (field simulation and laboratory) versus model for phenanthrene flux

contaminant fluxes from field and laboratory experiments occurred during the initial loading or placement stages (0-48 hr); followed by decreasing fluxes to low levels. Emissions also increased after sediment reworking in both the field and laboratory. Increasing the surface moisture of the IHC sediment did not result in increased fluxes under field or laboratory conditions. Measured contaminant emissions from the laboratory and field simulation experiments agreed well with model predictions. The model provided on ADDAMS can be used to generate initial screening data for maximum contaminant fluxes from freshly deposited dredged material. Actual volatile emission measurements may be required if management options, such as sediment reworking, for which the models are not designed, are planned.

POINTS OF CONTACT: This technical note was written by Ms. Cynthia Price, (601) 634-3621, pricec@wes.army.mil, Dr. James Brannon, (601) 634-3725, brannonj@wes.army.mil, Ms. Sally Yost, (601) 634-3622, yosts@wes.army.mil, Mr. R. Ravikrishna, (225) 388-4805 rravikr@unix1.sncc.lsu.edu, and Dr. K.T. Valsaraj, (225) 388-1426, valsaraj@che.lsu.edu. Questions regarding this technical note should be directed to Ms. Price or the manager of the Long-Term Effects of Dredging Operations Program, Dr. Robert M. Engler, (601) 634-3624, englerr@wes.army.mil.

REFERENCES

- Choy, B., and Reible, D. D. (1999). "Contaminant transport in soils and sediments: Mathematical analysis," Report to the Hazardous Substance Research Center (S&SW), Louisiana State University, Baton Rouge, LA, November.
- Price, C., Brannon, J., Myers, T., Valsaraj, K. T., Thibodeaux, L., and Reible, D. (1997). "Development of laboratory procedures to predict volatile losses from contaminated sediments," *Environmental Effects of Dredging Technical Notes Collection* (TN EEDP-02-23), U.S. Army Engineer Research and Development Center, Vicksburg, MS. www.wes.army.mil/el/dots/eedptn
- Price, C., Brannon, J., Yost, S., Valsaraj, K. T., and Ravikrishna, R. (1998). "Volatile losses from exposed sediment," *Environmental Effects of Dredging Technical Notes Collection* (TN EEDP-02-24), U.S. Army Engineer Research and Development Center, Vicksburg, MS. www.wes.army.mil/el/dots/eedptn
- Price, C., Brannon, J., Yost, S., Valsaraj, K. T., and Ravikrishna, R. (1999). "Volatile losses from aged field sediments," *Environmental Effects of Dredging Technical Notes Collection* (TN EEDP-02-26), U.S. Army Engineer Research and Development Center, Vicksburg, MS. www.wes.army.mil/el/dots/eedptn
- Price, R. A., Skogerboe, J. G., and Lee, C. R. (1998). "Predicting surface runoff water quality from upland disposal of contaminated dredged material," *Environmental Effects of Dredging Technical Notes Collection* (TN EEDP-02-25), U.S. Army Engineer Research and Development Center, Vicksburg, MS. www.wes.army.mil/el/dots/eedptn
- Ravikrishna, R., Valsaraj, K. T., Yost, S., Price, C. B., and Brannon, J. M. (1998). "Air emissions from exposed, contaminated sediment and dredged materials; 2, Diffusion from laboratory-spiked and aged field sediments," *Journal of Hazardous Materials* 60, 89-104.
- Thibodeaux, L. J. (1989). "Theoretical models for evaluation of volatile emissions to air during dredged material disposal with applications to New Bedford Harbor, Massachusetts," Miscellaneous Paper EL-89-3, U.S. Army Engineer Research and Development Center, Vicksburg, MS.
- U.S. Environmental Protection Agency. (1982). "Test methods for evaluating solid waste physical and chemical methods," SW-846, 2d ed., National Technical Information Service, Springfield, VA (NTIS No. PB87-120291).
- Valsaraj, K. T., Choy, B., Ravikrishna, R., Thibodeaux, L. J., Reible, D. D., Price, C., Brannon, J. M., and Myers, T. (1997). "Air emissions from contaminated sediments and dredged materials; 1, Experimental data in laboratory microcosms and mathematical modeling," *Journal of Hazardous Materials* 60, 65-87.

Valsaraj, K. T., Thibodeaux, L. J., and Reible, D. D. (1995). "Dredging, remediation, and containment of contaminated sediments," ASTM STP 1293, K. R. Demars, G. N. Richardson, R. N. Yong, and R. C. Chaney, eds., American Society for Testing and Materials, Philadelphia, PA, 227-238.

Valsaraj, K. T., Ravikrishna, R., Choy, B., Reible, D. D., Thibodeaux, L. J., Price, C. B., Yost, S., Brannon, J. M., and Myers, T. E. (1999). "Air emissions from exposed contaminated sediments and dredged materials," *Environmental Science and Technology* 33, 142-149.